

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

365-444P

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

09/530803
NEW

INTERNATIONAL APPLICATION NO.

PCT/EP98/07215

INTERNATIONAL FILING DATE

November 9, 1998

PRIORITY DATE CLAIMED

November 7, 1997

TITLE OF INVENTION

COLOURED POLYPROPYLENE COMPOSITIONS

APPLICANT(S) FOR DO/EO/US

CROZIER, Herve; FOLLAND, Rick

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(3)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(2)).
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☒ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.-1449 and International Search Report (PCT/ISA/210)
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:
 - 1.) PCT Request (PCT/RO/101)
 - 2.) PCT Demand (PCT/IPEA/401)
 - 3.) International Preliminary Examination Report (PCT/IPEA/409)
 - 4.) Zero (0) sheets of Formal Drawings

02/ REC 0 PCT/PIO 05 MAY 2000

| | | |
|---|---|--------------------------------------|
| U.S. APPLICATION NO. (if known, see 37 CFR 1.5) 09/530803 | INTERNATIONAL APPLICATION NO. PCT/EP98/07215 | ATTORNEY'S DOCKET NUMBER 365-444P |
|---|---|--------------------------------------|

17. ☒ The following fees are submitted:
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5):
Neither international preliminary examination fee (37 CFR 1.482)
nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO
and International Search Report not prepared by the EPO or JPO. **\$970.00**

International preliminary examination fee (37 CFR 1.482) not paid to
USPTO but International Search Report prepared by the EPO or JPO **\$840.00**

International preliminary examination fee (37 CFR 1.482) not paid to USPTO
but international search fee (37 CFR 1.445(a)(2)) paid to USPTO. **\$690.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO
but all claims did not satisfy provisions of PCT Article 33(1)-(4) **\$670.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO
and all claims satisfied provisions of PCT Article 33(1)-(4) **\$96.00**
ENTER APPROPRIATE BASIC FEE AMOUNT =

| CALCULATIONS | | PTO USE ONLY |
|--------------|--|--------------|
| | | |

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☒ 30
months from the earliest claimed priority date (37 CFR 1.492(e)).

| | | |
|----|---------------|--|
| \$ | 840.00 | |
| \$ | 130.00 | |

| CLAIMS | NUMBER FILED | NUMBER EXTRA | RATE |
|---|--------------|--------------|------------|
| Total Claims | 14 - 20 = | 0 | X \$18.00 |
| Independent Claims | 2 - 3 = | 0 | X \$78.00 |
| MULTIPLE DEPENDENT CLAIM(S) (if applicable) Yes | | | + \$260.00 |

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|----|---------------|--|
| \$ | 0 | |
| \$ | 0 | |
| \$ | 260.00 | |

TOTAL OF ABOVE CALCULATIONS =

| | | |
|----|----------------|--|
| \$ | 1230.00 | |
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Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity statement
must also be filed (Note 37 CFR 1.9, 1.27, 1.28).

| | | |
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| \$ | 0 | |
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SUBTOTAL =

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| \$ | 1230.00 | |
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Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(f)).

| | | |
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| \$ | 0 | |
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TOTAL NATIONAL FEE =

| | | |
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| \$ | 1230.00 | |
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Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **\$40.00** per property +

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| \$ | 0 | |
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TOTAL FEES ENCLOSED =

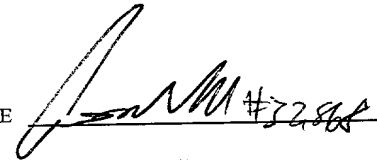
| | | |
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| \$ | 1230.00 | |
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| | Amount to be: refunded | \$ |
| | charged | \$ |

- a. ☒ A check in the amount of \$ **1230.00** to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account. No. _____ in the amount of \$ _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
overpayment to Deposit Account No. 02-2448.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

Send all correspondence to:
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#30,330 (LRS)
REGISTRATION NUMBER

09/530803

527 Rec'd PCT/PTO 05 MAY 2000

PATENT
365-444P

IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicant: CROZIER, Herve et al.
Int'l. Appl. No.: PCT/EP98/07215
Appl. No.: New Group:
Filed: May 5, 2000 Examiner:
For: COLOURED POLYPROPYLENE COMPOSITIONS

PRELIMINARY AMENDMENT

BOX PATENT APPLICATION

Assistant Commissioner for Patents
Washington, DC 20231

May 5, 2000

Sir:

The following Preliminary Amendments and Remarks are respectfully submitted in connection with the above-identified application.

AMENDMENTS

IN THE SPECIFICATION:

Please amend the specification as follows:

Before line 1, insert --This application is the national phase under 35 U.S.C. § 371 of PCT International Application No. PCT/EP98/07215 which has an International filing date of November 9, 1998, which designated the United States of America.--

IN THE CLAIMS:

Please amend the claims as follows:

Claim 6: Line 1, change "any of claims 1 to 5" to
--claim 1--

Claim 7: Line 1, change "any of claims 1 to 5" to
--claim 1--

Claim 8: Line 1, change "any of the preceding claims" to
--claim 1--

Claim 12: Line 1, change "any of claims 1 to 9" to
--claim 1--

REMARKS

The specification has been amended to provide a cross-reference to the previously filed International Application. The claims have also been amended to delete the improper multiple dependencies and to place the application into better examination. Entry of the present amendment and favorable action on the above-identified application are respectfully requested.

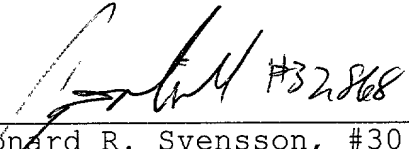
If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional

Docket No. 365-444P

fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17;
particularly, extension of time fees.

Respectfully submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

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(Rev. 04/19/2000)

COLOURED POLYPROPYLENE COMPOSITIONS**Background of the Invention****Field of the Invention**

The present invention relates to coloured polymer compositions. In particular, the present invention concerns compositions of propylene homo- and copolymers suitable for caps and closures and similar polymer articles. The invention also concerns a process for preparing such compositions. Finally, the present invention relates to the use of the new propylene polymers or copolymers for the manufacture of products by melt stage processing, e.g., by blow moulding, thermoforming, injection moulding and sheet or film extrusion.

Description of Related Art

To an increasing extent, caps and closures of various design for drinks, food, household, hygiene, health-care, oils and chemicals and other applications are nowadays manufactured from polymeric materials. This is partly due to the requirement for high productivity, i.e. short processing cycle, which becomes crucial for the mass production of carbonated soft drinks caps that are usually obtained by either injection moulding or compression moulding techniques.

Propylene homo- and copolymers having excellent resistance to heat and chemicals as well as attractive mechanical properties, such as stiffness and impact resistance, are becoming a particularly interesting materials for these applications.

There are, however, some problems related to the prior art. Thus, nearly all caps and closures manufactured from polymeric materials are coloured. It has been experienced that pigments may have a nucleating effect on polypropylene and variation in intensity of this effect from one colour to another will result in dimensional variations because of differences in the shrinkage associated with the nucleation.

Summary of the Invention

It is an object of the present invention to eliminate the problems related to the prior art and to provide novel coloured polypropylene compositions having consistent shrinkage and improved mechanical properties highly suited to the manufacture of injection moulded or compression moulded products which can be used as caps and closures.

A second object of the invention is to provide a process for preparing novel polypropylene compositions of the above kind.

It is still a further object of the present invention to provide products of polypropylene compositions by injection moulding or compression moulding techniques.

These and other objects, together with the advantages thereof over known processes and products, which shall become apparent from the specification which follows, are accomplished by the invention as hereinafter described and claimed.

The invention is based on blending colouring pigments with propylene homo- or copolymers nucleated for high crystallinity. In connection with the present invention it has been found that nucleating the PP resin may reduce the differences between the various degrees of shrinkage of polymer compositions coloured with different pigments. However, conventional inorganic or organic nucleating agents, e.g. talc, are either too weak to have a dominating effect or they can give rise to undesired reactions with the pigments. The conventional agents can also be difficult to disperse and there can be restrictions on food contact approvals (e.g. NaBz). Some are non-economical (e.g. sorbitol derivatives) for use for PP for caps and closures.

According to the present invention, the pigments are therefore blended with propylene polymers or copolymers nucleated with polymeric vinyl compounds to provide coloured polypropylene compositions having a consistent shrinkage during melt processing irrespective of the colouring pigment used.

The use of vinyl compounds, such as polymers of vinyl cycloalkanes and 3-methyl-1-butene, as nucleating agents in the form of reactor made blends of polypropylene and polymerised vinyl compounds or polypropylene compounds, is suggested in the prior art, cf. EP Patent Specifications Nos. 0 152 701, 0 151 883, 0 368 577 and 0 417 319.

5 However, none of the prior art publications makes any reference to the use of these highly nucleated materials for the production of coloured caps and closures.

According to the present invention it has now surprisingly been found that propylene homo- or copolymers nucleated with a component containing polymerized vinyl compound units will give excellent dimensional consistency by dominating the pigments' nucleating effect with its strong nucleation. The strongly nucleating effect of the polymeric nucleating agent is apparent from the high crystallisation temperature of the polymer. Thus, the crystallisation temperature of the material is at least 7 °C, preferably 10 °C and in particular over 13 °C higher than the crystallisation temperature of the corresponding non-nucleated polymer and the material exhibits a fast crystallisation rate. Caps of various colours moulded with a polypropylene nucleated with a polymerised vinyl compound grade to provide a composition according to the present invention will therefore have practically the same dimensions.

20 More specifically, the polymer composition according to the present invention is characterized by what is stated in the characterizing part of claim 1.

The process according to the present invention for preparing coloured polypropylene compositions is characterized by what is stated in the characterizing part of claim 10.

25 The present compositions can be used in any kind of polymer articles. Particular advantages are obtained by applying the compositions to the manufacture of injection moulded and/or compression moulded products as well as articles produced by thermoforming, blow moulding and film and sheet extrusion.

30 The invention achieves a number of considerable advantages. In particular it should be pointed out that the strong nucleating effect of a polymeric nucleating agent containing

polymerized vinyl compound units will give potential for cycle time reduction because solidification in the mould will happen earlier and faster compared to any other PP grade nucleated with conventional nucleating agents. There are also other benefits of the present invention compared to the use of additive nucleating agents that are of particular interest for the manufacture of caps and closures: the invention will provide for a reduction of the number and amount of additives. The polymeric nucleating agents are inert towards other additives/pigments, they give no taste and odour, no migration / plate out, excellent dispersion of the nucleating effect and more consistent nucleation. These positive effects are accompanied with clearly smaller amounts of the polymeric nucleating agents compared to additive nucleation.

The characteristics of the polymer compositions can easily be tailored in respect to MFR, type of polymer (homopolymer, copolymer, impact modified ...) as well as in respect to physical properties.

Next, the invention will be more closely examined with the aid of the following detailed description.

Detailed Description of the Invention

The compositions of the present invention include a polymeric component comprising a propylene polymer nucleated with polymerized vinyl compounds together with at least one colouring agent. The compositions can contain other components known in the art, such as adjuvants, additives and fillers.

The colouring agent used in the present invention can be any colouring pigment, organic or inorganic, having a nucleating effect of various strength on propylene homo- or copolymers. By dominating the nucleating effect, if any, of the pigment, the nucleated propylene homo- or copolymer will provide a controlled and predictable shrinkage irrespective of the pigment.

Examples of colouring pigments are white pigments, such as titanium dioxide,

yellow/orange pigments such as isoindolinone or azocondensation, red/violet such as quinacridone or diketo pyrrolo pyrol, blue/green pigments such as ultramarine blue or Cu Phtalocyanine blue, and black pigments such as carbon black. The amount of pigments is usually 0.01 to 5 % by weight of the polypropylene component.

5

For the purpose of the present invention, the terms "colouring agent" and "colouring pigment" are interchangeably used for designating any material used to give the final product a desired colour which is different from the one it would have without the use of that specific material.

10

The main component of the present compositions is the nucleated propylene polymer which contains a polymerized vinyl compound in an amount of 0.0001 to 1 %, in particular about 5 to 1000 ppm, by weight of the composition. By this nucleation it is possible to attain a polypropylene having a high degree of crystallinity, a high crystallization temperature, small crystal size and a great crystallization rate. These kinds of compositions can be used for the preparation of moulded products. They exhibit improved optical and physical properties.

15

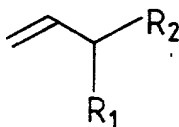
The nucleation of the propylene polymers can be carried out by modifying the polymerization catalyst with vinyl compounds and using the modified catalyst for polymerization of propylene optionally in the presence of comonomers to provide a propylene homopolymer or copolymer containing about 0.0001 to 1 % (calculated from the weight of the composition) polymerized vinyl compounds. Another approach for nucleating propylene polymers comprises blending polypropylene with polymers containing vinyl compound units.

20

25

For the purpose of the present invention "vinyl compounds" are compounds having the formula I

30



wherein R_1 and R_2 together form a 5 or 6 membered saturated or unsaturated or aromatic ring or they stand independently for a lower alkyl comprising 1 to 4 carbon atoms.

The following specific examples of vinyl compounds can be mentioned: vinyl
5 cycloalkanes, in particular vinyl cyclohexane, vinyl cyclopentane, vinyl-2-methyl
cyclohexane and vinyl norbornane, 3-methyl-1-butene, styrene, p-methyl-styrene, 3-ethyl-
1-hexene or mixtures thereof. Vinyl cyclohexane (VCH) is a particularly preferred
monomer but, for example, 3-methyl-1-butene can be used as a monomer or comonomer to
adjust the crystallisation temperature.

10

For the purpose of the present invention "nucleated propylene polymer" stands for a
polymer having an increased and controlled degree of crystallinity preferably amounting to
over 50 % and preferably having a crystallization temperature of more than 7 °C,
preferably over 10 °C and in particular over 13 °C of the T_c of the corresponding non-
15 nucleated polymer. Using $MgCl_2$ -supported high-yield Ziegler-Natta catalysts
crystallization temperatures of more than 120 °C, preferably over 124 °C and in particular
over 126 °C can be obtained. In compositions containing colouring pigments having a
nucleating effect, particularly advantageous results are obtained by using polymers having
a crystallization temperature over 15 °C higher than that of the corresponding non-
20 nucleated polymer (for a polymer produced with the above-mentioned ZN-catalyst, 128
°C).

20

According to a preferred embodiment of the present invention, modification of the catalyst
by polymerizing a vinyl compound, such as VCH, in the presence thereof is performed in
25 an inert fluid which does not dissolve the polymer formed (e.g. polyVCH). One
particularly preferred polymerization medium comprises a viscous substance, in the
following a "wax", such as an oil or a mixture of an oil with a solid or semi-solid polymer
(oil-grease). The viscosity of such a viscous substance is usually 1,000 to 15,000 cP (1 - 15
Ns/m²) at room temperature. The advantage of wax prepolymerization is that the catalyst
30 can be prepolymerized, stored and fed into the process in the same media and catalyst wax
preparation and prepolymerization is performed in the same process device. Due to the
fact that no washing, drying, sieving and transferring thus are needed, the catalyst activity

30

is maintained (cf. Finnish Patent No. 95387). The present process is inexpensive because high catalyst concentrations and high PP production capacities can be used. Also the amount of waste is diminished because the medium used during polymerization of the vinyl compound does not have to be removed.

5

According to another preferred embodiment, the method for improving the crystallinity and transparency of polypropylene by blending a crystalline polypropylene with a vinyl cycloalkane polymer is carried out by melt-kneading the crystalline polypropylene with the crystal nucleating agent, compounding the crystal nucleating agent or reactor made blend of the crystal nucleating agent and PP with the crystalline polypropylene and melt kneading the mixture during film formation, and compounding the master batch of the crystal nucleating agent with the crystalline polypropylene.

10

The vinyl compound units of the blending and compounding process can be derived from any of the units identified in the above formula I in connection with the first embodiment of the invention.

15

As catalyst any stereospecific catalyst for propylene polymerization can be used, which is capable of catalyzing polymerization and copolymerization of propylene and comonomers at a pressure of 10 to 100 bar, in particular 25 to 80 bar, and at a temperature of 40 to 110 °C, in particular 60 to 110 °C. Ziegler-Natta as well as metallocene catalysts can be used.

20

Generally, the Ziegler-Natta catalyst used in the present invention comprises a catalyst component, a cocatalyst component, an external donor, the catalyst component of the catalyst system primarily containing magnesium, titanium, halogen and an internal donor.

25

Examples of suitable catalyst systems are described in, for example, Finnish Patents Nos. 86866, 96615 and 88047 and 88048.

30

One particularly preferable catalyst, which can be used in the present invention, is disclosed in FI Patent No. 88047. Another preferred catalyst is disclosed in Finnish Patent Application No. 963707.

A catalyst system useful in the present process can be prepared by reacting a magnesium halide compound with titanium tetrachloride and an internal donor. The magnesium halide compound is, for example, selected from the group of magnesium chloride, a complex of magnesium chloride with a lower alkanol and other derivatives of magnesium chloride.

- 5 MgCl_2 can be used as such or it can be combined with silica, e.g. by absorbing the silica with a solution or slurry containing MgCl_2 . The lower alkanol used can be preferably methanol or ethanol, particularly ethanol.

10 The titanium compound used in the preparation of the procatalyst is preferably an organic or inorganic titanium compound, having an oxidation state of titanium of 3 or 4. Also other transition metal compounds, such as vanadium, zirconium, chromium, molybdenum and tungsten compounds can be mixed with the titanium compound. The titanium compound usually is halide or oxyhalide, an organic metal halide, or a purely metal organic compound, in which only organic ligands have been attached to the transition metal.

- 15 Particularly preferable are the titanium halides, especially TiCl_4 . Preferably the titaniation is carried out in two or three steps.

20 The Ziegler-Natta catalyst used can also be an heterogeneous unsupported TiCl_3 based catalyst. This kind of catalysts are typically solid TiCl_3 in a delta crystalline form which are activated with aluminium-chloride-alkyls, such as diethylaluminiumchloride. The solid TiCl_3 catalyst are typically prepared by reduction of TiCl_4 with aluminium-alkyls and/or aluminium-chloride-alkyls, possibly combined with heat treatment to maximise the desired delta crystalline form of TiCl_3 . The performance, especially stereospecificity, of these catalyst can be improved by using Lewis-bases (electron donors), such as esters, ethers or

25 amines.

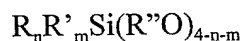
30 The activity and stereospecificity of these heterogeneous unsupported TiCl_3 based catalysts are typically so low that propylene polymers or copolymers prepared require purification from catalyst residues and removal of some atactic non-crystalline polymer.

The alkoxy group of the phthalic acid ester used comprises at least five carbon atoms, preferably at least 8 carbon atoms. Thus, as the ester can be used for example propylhexyl

phthalate, dioctyl phthalate, dinonyl phthalate, diisodecyl phthalate, di-undecyl phthalate, ditridecyl phthalate or ditetradecyl phthalate.

The partial or complete transesterification of the phthalic acid ester can be carried out e.g. by selecting a phthalic acid ester - a lower alcohol pair, which spontaneously or with the aid of a catalyst, which does not damage the procatalyst composition, transesterifies the catalyst at an elevated temperatures. It is preferable to carry out the transesterification at a temperature, which lies in the range of 110 to 150 °C, preferably 120 to 140 °C.

The catalyst prepared by the method above is used together with an organometallic cocatalyst and with an external donor. Generally, the external donor has the formula IV



wherein

R and R' can be the same or different and they stand for a linear, branched or cyclic aliphatic, or aromatic group;

R'' is methyl or ethyl;

n is an integer 0 to 3;

m is an integer 0 to 3; and

n+m is 1 to 3.

The aliphatic groups in the meanings of R and R' can be saturated or unsaturated. Linear C₁ to C₁₂ hydrocarbons include methyl, ethyl, propyl, butyl, octyl and decanyl. As examples of suitable saturated branched C₁₋₈ alkyl groups, the following can be mentioned: isopropyl, isobutyl, isopentyl, tert-butyl, tert-amyl and neopentyl. Cyclic aliphatic groups containing 4 to 8 carbon atoms comprise, e.g., cyclopentyl, cyclohexyl, methyl cyclopentyl and cycloheptyl.

A group of interesting donors is formed by strongly co-ordinating donors which form relatively strong complexes with catalyst surface, mainly with MgCl₂ surface in the presence of aluminium alkyl and TiCl₄. The donor components are characterised by a

strong complexation affinity towards catalyst surface and a sterically large and protective hydrocarbon (R'). Such external donors can be selected from the group consisting of dicyclopentyl dimethoxysilane, diisopropyl dimethoxysilane, di-isobutyl dimethoxysilane, and di-t-butyl dimethoxysilane.

5

An organoaluminum compound is used as a cocatalyst. The organoaluminium compound is preferably selected from the group consisting of trialkylaluminium, dialkyl aluminium chloride and alkyl aluminium sesquichloride.

10 The metallocene catalyst comprises a metallocene/activator reaction product impregnated in a porous support at maximum internal pore volume. The catalyst complex comprises a ligand which is typically bridged, and a transition metal of group IVA...VIA, typically a metal halide, and aluminium alkyl. The ligands can belong to group of heterocyclic substituted or unsubstituted compounds, e.g. indocenes, naftenes, or any other bulky

15 compound which can control the stereoselectivity of the catalyst especially when ligands are bridged together with silane or other chemical bond. The activator is selected from a group in which are derivatives of water and aluminium alkyls e.g. trimethyl aluminium, triethyl aluminium, and tri t-butyl aluminium, or another compound capable of activating the complex. The metallocene/activator reaction product, a solvent capable of dissolving it,

20 and a porous support are brought into mutual contact, the solvent is removed and the porous support is impregnated with the metallocene/activator reaction product, the maximum amount of which corresponds to the pore volume support, cf. International PCT Application No. PCT/FI94/00499.

25 One typical structure of metallocene compound is bridged bis(2-R-4-R'-indenyl) M Cl₂, wherein both R and R' are aliphatic, cycloaliphatic or aromatic hydrocarbons having 1 to 18 C atoms, R' is typically phenyl or naphthyl, and R is typically methyl or ethyl. M is a transition metal, typically titanium, zirconium or hafnium. R and R' may contain heteroatoms, such as silicon, nitrogen, phosphorous or germanium. The bridge between the

30 indenyls is made from 1 to 3 atoms, such as carbon, silicon, nitrogen, phosphorous or germanium. A typical bridge is dimethylsilyl or ethyl. An example of such a metallocene compound is dimethylsilyl-bis(2-methyl-4-phenyl-indenyl)zirconium dichloride.

Following the modification of the catalyst with the vinyl compound of the first preferred embodiment of the invention, the catalyst is optionally prepolymerized with propylene and/or another 1-olefin to provide a prepolymerized catalyst composition which is used for polymerization of propylene optionally together with comonomers.

5

The propylene homo- or copolymer can have a unimodal or bimodal molar mass distribution. Thus, the equipment of the polymerization process can comprise any polymerization reactors of conventional design for producing propylene homo- or copolymers. For the purpose of the present invention, "slurry reactor" designates any reactor, such as a continuous or simple batch stirred tank reactor or loop reactor, operating in bulk or slurry and in which the polymer forms in particulate form. "Bulk" means a polymerization in reaction medium that comprises at least 60 wt-% monomer. According to a preferred embodiment the slurry reactor comprises a bulk loop reactor. By "gas phase reactor" is meant any mechanically mixed or fluid bed reactor. Preferably the gas phase reactor comprises a mechanically agitated fluid bed reactor with gas velocities of at least 0.2 m/sec.

10

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Thus, the polymerization reactor system can comprise one or more conventional stirred-tank slurry reactors, as described in WO 94/26794, or one or more gas phase reactors. Preferably the reactors used are selected from the group of loop and gas phase reactors and, in particular, the process employs at least one loop reactor and at least one gas phase reactor. This alternative is particularly suitable for producing bimodal poly-propylene. By carrying out the polymerization in the different polymerization reactors in the presence of different amounts of hydrogen, the MWD (molecular mass distribution) of the product can be broadened and its mechanical properties improved. It is also possible to use several reactors of each type, e.g. one loop reactor and two or three gas phase reactors or two loop reactors and one gas phase reactor, in series.

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In every polymerization step it is possible to use also comonomers selected from the group of ethylene, propylene, butene, pentene, hexene and alike as well as their mixtures.

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In addition to the actual polymerization reactors used for producing the propylene homo-

or copolymer, the polymerization reaction system can also include a number of additional reactors, such as pre- and/or postreactors. The prereactors include any reactor for prepolymerizing the catalyst with propylene and/or other 1-olefins. The postreactors include reactors used for modifying and improving the properties of the polymer product.

5 All reactors of the reactor system are preferably arranged in series.

The gas phase reactor can be an ordinary fluidized bed reactor, although other types of gas phase reactors can be used. In a fluidized bed reactor, the bed consists of the formed and growing polymer particles as well as still active catalyst come along with the polymer
10 fraction. The bed is kept in a fluidized state by introducing gaseous components, for instance monomer on such flowing rate which will make the particles act as a fluid. The fluidizing gas can contain also inert carrier gases, like nitrogen and also hydrogen as a modifier. The fluidized gas phase reactor can be equipped with a mechanical mixer.

15 The gas phase reactor used can be operated in the temperature range of 50 to 115 °C, preferably between 60 and 110°C and the reaction pressure between 5 and 50 bar and the partial pressure of monomer between 2 and 45 bar.

The pressure of the effluent, i.e. the polymerization product including the gaseous reaction
20 medium, can be released after the gas phase reactor in order optionally to separate part of the gaseous and possible volatile components of the product, e.g. in a flash tank. The overhead stream or part of it is recirculated to the reactor.

The propylene homo- or copolymer produced preferably has a MWD of 2 - 10 and a MFR₂
25 in the range of 0.01 - 1500 g/10 min., in particular 0.05 - 500 g/10 min. MFR₂ values disclosed herein are measured according to ISO 1133, 230 °C, using 2.16 kg load.

In the second embodiment of the invention, wherein a uni- or bimodal propylene homo- or copolymer is blended and compounded with a polymer comprising vinyl compound units,
30 the blending is carried out as known in the art using said nucleating polymeric agent.

By means of both embodiments, a propylene homopolymer or copolymer is produced with

high-yield Ziegler-Natta catalysts, having high stiffness, an increased overall degree of crystallization and a crystallization temperature of the propylene homopolymer fraction of more than 120 °C, preferably over 124 °C and in particular over 126 °C. The degree of crystallization for a propylene homopolymer is generally over 48 %, and often over 50 %.

5

The amount of the nucleating polymeric agent is, in case of propylene polymers or copolymers, about 0.0001 to 1 wt-%, and in case of polypropylene blends about 0.0001 to 0.5 wt-%.

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This nucleated polypropylene (100 parts by weight) is blended with 0.01 to 5 parts by weight of the coloured pigment of choice. The particle size of the pigment is usually 0.01 to 1000 micrometre and more often 0.1 to 10 micrometre.

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The colouring agent is usually in the form of a masterbatch comprising also a polymer carrier. The blending with the polypropylene is directly done at the conversion machine (e.g. extruder, injection moulding machine...) by dosing the pigment with a gravimetric side feeder. When the colouring agent is liquid it is dosed with a liquid pump.

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The present polymers and copolymers of propylene can be blended and optionally compounded with additives and adjuvants conventionally used in the art. Thus, suitable additives include antistatic agents, flame retardants, light and heat stabilizers, reinforcement agents, pigments and carbon black. Fillers such as mica, CaCO_3 , talc and wollastonite can also be used. Further, the polymers and copolymers can be blended with non-nucleated propylene and/or with other polymers, in particular other polyolefins, such as LD-, LLD-, MD- and HD-polyethylenes and polybutylene.

25

Compositions according to the invention containing pigments will exhibit very small variation in shrinkage irrespective of the colouring agent used. As the results indicated below in Table 1 show, the variation in shrinkage in both flow and cross direction is less than 5 % for white, red and blue pigments compared to conventional, non-nucleated polymers having a variation of shrinkage in the range of 10 to 20 %. The fact that the pigments' nucleating effect is clearly dominated by the nucleated polypropylene with its

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strong nucleation is apparent from the results showing that the shrinkage is practically constant irrespective of whether or not the compositions contain any colouring pigment at all. This feature is rather surprising in particular when comparing the shrinkage of the present compositions to conventional talc-nucleated homopolymer compositions which have the same variation as non-nucleated polymer compositions (or even greater) in transversal direction to the flow.

The homopolymer or copolymer composition thus obtained can be used for the manufacture of moulded articles, in particular articles processed by blow moulding, injection moulding, compression moulding, thermoforming and sheet or film extrusion, pipe and cable extrusion.

Particularly useful products include caps and closures for various food, in particular carbonated soft drinks, household, hygiene, health-care and other applications. Further interesting products and articles include bottles, containers and pails.

Examples

The following non-limiting examples illustrate the invention.

Example 1

Catalyst modification with polymerisation of vinyl cycloalkane:

A high yield MgCl_2 supported TiCl_4 Ziegler-Natta catalyst prepared according to Finnish patent FI 88047 was dispersed into a mixture of oil and crease (Shell Ondina Oil N 68 and Fuchs Vaseline Grease SW in 3.2:1 Oil/grease volume ratio). The titanium content of the catalyst was 2.5 wt-%, and the concentration of the catalyst in oil-grease mixture was 176 g cat/dm³. Triethylaluminium (TEAL) was added to the catalyst dispersion in a TEAL to titanium mole ratio of 1.5. After that vinylcyclohexane (VCH) was added to the reaction mixture, and the VCH to catalyst weight ratio was 1:1. The reaction mixture was mixed in a temperature of 55 °C until the concentration of unreacted VCH in the reaction mixture

was 350 ppm by weight.

Example 2

Polymerisation of propylene

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The modified catalyst in the oil grease mixture (catalyst mud) obtained from example 1, TEAL, dicyclopentyl dimethoxysilane and propylene were continuously fed to a process consisting of a prepolymerisation reactor and a loop reactor.

10

Before mixing, the TEAL and dicyclopentyl dimethoxysilane in a 10.7 w/w ratio was contacted with the catalyst mud. After that the mixture was transferred with propylene, containing the desired amount of hydrogen as molecular weight regulating agent, to a continuous, stirred prepolymerisation reactor. After the prepolymerisation, the reaction mixture together with additional propylene and hydrogen was fed to a continuous loop reactor operating at 68 °C. The obtained PP homo-polymer-propylene slurry containing the catalyst was continuously recovered from the loop reactor to a flashing unit where the liquid propylene was vaporised and the remaining solid polymer particles were continuously recovered from the flashing unit. After purging the unreacted monomers, the required stabilisers and other additives were added and the polymer powder was pelletised with an extruder.

15

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The final polymer had an MFR₂ of 25 g/10 min, and insolubles in boiling n-heptane 96.0 wt-%.

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Example 3

Dimensional consistency

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The PP homopolymer described in previous examples and a commercial non nucleated PP homopolymer (MFR 12) and a commercial talc-nucleated PP homopolymer (MFR35) were moulded by injection moulding (machine: Netstal 300 tons, N1570/300MPS) in the form of a box bac characterised by:

- thickness: 1.8 mm

- length: 370 mm
 - width: 185 mm
 - height: 95 mm
 - injection: cold runner
- 5 • max flow length: 300 mm

4 preparations for each of the 3 polypropylenes were moulded:

1. natural
2. 100 parts by weight + 2 parts by weight of white masterbatch (titanium dioxide based
10 white pigment)
3. 100 parts by weight + 2 parts by weight of red masterbatch (quinacridone based red
pigment)
4. 100 parts by weight + 2 parts by weight of dark blue masterbatch (Cu Phtalocyanine
blue based blue pigment)

15 The preparations were blended batch-wise in a bag to prepare roughly 5 kg for each.

Typical moulding conditions were:

- Injection speed: 100 mm/sec
- Holding pressure: 300 bar
- 20 • holding pressure time: 12 sec
- cooling time: 15 sec
- cycle time: 35 sec

25 Dimension of the boxes were measured with an optical device between lines of grid both in
flow and in transverse direction.

Shrinkage, reported in Table 1, is calculated by comparing the dimension measured to the
nominal mould dimension. The cross direction has proved to be determinant in
characterising the shrinkage behaviour of a PP material.

30

Table 1. Shrinkage (%) measured on injection moulded boxes of constant weight

| | Grade | Colour | Shrinkage (%) | |
|----|-------------------------------|-----------|----------------|-----------------|
| | | | Flow direction | Cross direction |
| 5 | Homopolymer of Example 2 | Natural | 1.68 | 1.90 |
| | | White | 1.68 | 1.95 |
| | | Red | 1.70 | 1.93 |
| | | Blue | 1.70 | 1.90 |
| | | Delta Max | 0.02 | 0.05 |
| 10 | Non-nucleated PP homopolymer | Natural | 1.71 | 1.58 |
| | | White | 1.63 | 1.64 |
| | | Red | 1.71 | 1.74 |
| | | Blue | 1.79 | 1.96 |
| | | Delta Max | 0.16 | 0.38 |
| 15 | Talc-nucleated PP homopolymer | Natural | 1.59 | 1.54 |
| | | White | 1.62 | 1.55 |
| | | Red | 1.63 | 1.71 |
| | | Blue | 1.63 | 1.96 |
| | | Delta Max | 0.04 | 0.41 |

The non-nucleated PP homopolymer shrank to different extent with different colours. That also attested the different nucleating effect of the different pigments which were also confirmed by measuring crystallisation temperatures of the coloured boxes which were 115.8 °C, 115.7 °C, 119.5 °C and 129.3 °C for the natural, white, red, and blue respectively. Crystallisation temperature was measured by differential scanning calorimetry by weighting 3 mg sample placed in a furnace heated at 10 °C/min from room temperature to 220 °C and then cooled at 10 °C/min to room temperature to get the crystallisation exothermic peak from which the maximum gives the crystallisation temperature.

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The talc-nucleated PP homopolymer behaved similarly to the non-nucleated PP homopolymer in the ESNs that shrinkage also varied a lot depending on the colour.

The PP homopolymer (related to the present invention) exhibited practically the same shrinkage, hence the same box dimension, for all the preparations.

Example 4

5 Cycle time

The three PP homopolymer samples mentioned in Example 3 were injection moulded in the form of caps on a Netstal 120 tons, HP 1200/445. The mould was a 3 plate mould with 4 cavities, and unscrewing of the cap's threads. The caps were oval, with inner threads, with a hinged flip top. Dimension were: length 50 mm, height 30 mm, width 38 mm, wall thickness 1.2 mm.

Table 2 indicates the moulding parameters.

15 **Table 2. Moulding parameters**

| | | PP homopolymer of Example 2 | non-nucleated PP homopolymer | talc-nucleated PP homopolymer |
|--------------------------|-------------|--------------------------------|---------------------------------|----------------------------------|
| MFR | g/10 min | 25 | 12 | 35 |
| injection speed | mm/ min | 50 | 50 | 50 |
| holding pressure | bar | 300 | 500 | 300 |
| holding pressure time | sec | 3 | 3 | 3 |
| cooling time | sec | 9 | 11.5 | 10.5 |
| CYCLE TIME | SEC | 18.5 | 21 | 20 |

25

The polypropylene nucleated with a polymerised vinyl compound could be moulded with faster cycle because it started to freeze (crystallise) in the mould earlier and faster than the non-nucleated and talc-nucleated PP homopolymers. Shortest cycle time was determined by decreasing cooling time until the caps deformed at ejection because they were not solidified enough.

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Example 5

Dimensional consistency

The three PP homopolymer samples of Example 3 were also injection moulded according to Example 4. The conditions were identical except for the cooling time which was 11.5 seconds for all them, for the natural but also with red and blue coloured specimens prepared as described in Example 3.

Shrinkage was measured with the height of the caps, compared to the nominal dimension.

Table 3. Shrinkage in %

| | Natural | Red | Blue |
|-------------------------------|---------|------|------|
| PP homopolymer of Example 2 | 1.80 | 1.80 | 1.80 |
| non-nucleated PP homopolymer | 1.25 | 1.41 | 1.71 |
| talc-nucleated PP homopolymer | 1.35 | 1.41 | 1.71 |

As observed in Example 3, the polypropylene nucleated with a polymerised vinyl compound is superior to the non-nucleated and the talc-nucleated PP homopolymers in the sense that shrinkage, hence dimension, was equal for natural, red and blue caps. On the other hand, variation was observed in dimension for the non-nucleated and talc-nucleated natural, red, and blue caps.

IN THE CLAIMS:

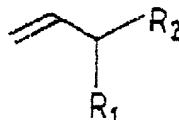
1. Coloured polymer composition comprising

- a propylene polymer nucleated with a polymerized vinyl compound and having an at least 7 °C higher crystallization temperature than that of the corresponding non-nucleated polymer, and
- a colour pigment having a concentration of 0.01 to 5 wt-% calculated from the weight of the nucleated propylene polymer.

2. The composition according to claim 1, wherein the colour pigment has a nucleating effect on the propylene polymer.

3. The composition of claim 1 or 2, wherein the shrinkage of the composition, calculated by comparing the measured dimension of an injection moulded box with the nominal mould dimension, varies less than 5 % for different colour pigments.

4. The polymer composition according to claim 1, wherein the propylene polymer contains about 0.0001 to 1 % by weight of units derived from a vinyl compound of the formula



wherein R₁ and R₂ together form a 5 or 6 membered saturated or unsaturated or aromatic ring or they stand independently for a lower alkyl comprising 1 to 4 carbon atoms.

5. The polymer composition according to claim 4, wherein the propylene polymer contains cycloalkane units, in particular vinyl cyclohexane, vinyl cyclopentane, vinyl-2-methyl cyclohexane and vinyl norbornane, 3-methyl-1-butene, styrene, p-methyl-styrene or 3-ethyl-hexene units or mixtures thereof.

6. The polymer composition according to any of claims 1 to 5, wherein the nucleated

propylene polymer comprises a propylene polymer copolymer polymerized in the presence of a catalyst modified with a polymer containing vinyl compound units.

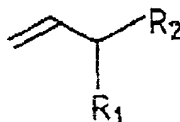
7. The polymer composition according to any of claims 1 to 5, wherein the nucleated
5 propylene polymer comprises a propylene homo- or copolymer blended with a polymer containing polymerised vinyl compound units.

8. The polymer composition according to any of the preceding claims, wherein the
10 pigment is selected from the group of white pigments, yellow/orange pigments, red/violet pigments, blue/green pigments and carbon black.

9. The polymer composition according to claim 8, wherein the pigment is selected from
the group of titanium dioxide, isoindolinone, azocondensation, quinacridone, diketo
pyrrole pyrrol, ultramarine blue, Cu Phtalocyanine blue and carbon black.

10. A process for preparing a coloured polymer composition comprising a propylene
15 polymer and a colour pigment, characterized by using a propylene polymer nucleated with a polymerized vinyl compound and having an at least 7 °C higher crystallization temperature than the corresponding non-nucleated polymer. the concentration of the
20 colouring pigment being 0.01 to 5 wt-% calculated from the weight of the nucleated propylene polymer.,.

11. The process according to claim 10 wherein 100 parts by weight of a nucleated
polypropylene composition containing about 0.0001 to 1 % by weight of units derived
25 from a vinyl compound of the formula



30 wherein R₁ and R₂ together form a 5 or 6 membered saturated or unsaturated or aromatic

ring or they stand independently for a lower alkyl comprising 1 to 4 carbon atoms is
 blended with 0.01 to 5 parts by weight of a colouring pigment selected from the group of
 white pigments, green pigments, red pigments, blue pigments and carbon black, to provide
 a coloured polypropylene composition, the shrinkage of which varies less than 5 % for
 5 different colour pigments, said shrinkage being calculated by comparing the measured
 dimension of an injection moulded box with the nominal mould dimension.

12. Use of a polymer composition according to any of claims 1 to 9 for the manufacture of
 polymer articles by injection moulding or compression moulding, thermoforming, blow
 10 moulding, film or sheet extrusion, pipe or cable extrusion.

13. The use of claim 12, wherein caps and closures for food, household, hygiene and
 health-care applications are manufactured.

(57) Abstract

The present invention concerns coloured polymer compositions and a process for the preparation thereof. The present composition comprise a propylene polymer nucleated with a polymeric nucleating agent containing vinyl compound units and having an at least 7 °C higher crystallization temperature than that of the corresponding non-nucleated polymer, and a colour pigment having a nucleating effect on the propylene polymer. The shrinkage of the composition varies less than 5 % for different colour pigments.